Atomic layer epitaxy of rare earth oxide films on GaAs(111)A and their device properties

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Yiqun Liu[1)*], Min Xu[2)], Jaeyeong Heo[1)], Peide D. Ye[2)], and Roy G. Gordon[1)**]

1) Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts, U.S.A.

2) School of Electrical and Computer Engineering, Purdue University, West Lafayette, Indiana, U.S.A.

Email:* yiqunliu@fas.harvard.edu, ** gordon@chemistry.harvard.edu

The aggressive scaling of MOSFETs has created interest in using high-mobility III-V channel materials to replace traditional strained Si. However, it has been challenging to form high-κ dielectrics that can passivate III-V surfaces with a low interface state density (D_{it}). We deposited $LaLuO_3$ high-κ dielectric layer by ALD on sulfur-passivated GaAs substrates. The precursors lanthanum tris(*N,N′*-diisopropylformamidinate), and lutetium tris(*N,N′*-diethylformamidinate) reacted with water vapor at 350 °C. The compositional ratio of La:Lu was about 1:1 by using one cycle of La_2O_3 followed by one cycle of Lu_2O_3 in one complete cycle of $LaLuO_3$. Both high-resolution XRD analysis and TEM showed that ALD $LaLuO_3$ formed epitaxially on GaAs(111)A substrates, as shown in Figures 1 and 2, respectively. The epitaxial layer exhibited a cubic structure with a lattice constant smaller than GaAs by 3.8%. The $LaLuO_3$ film had a high degree of crystalline perfection and was relaxed and not strained. Electrical characterizations showed the measured dielectric constant of around 30, which is close to its bulk crystalline value. The interface had a low interface state density (D_{it}) of ~7×10^{11} $cm^{-2}eV^{-1}$. The amount of lattice mismatch can be engineered by choosing various rare-earth oxides. ALD La_2O_3 formed cube-on-cube epitaxy on GaAs(111)A with a lattice constant just +0.9% larger than that of the substrate. The mismatch can be reduced to zero by adding some Y_2O_3 to the La_2O_3, using yttrium tris(*N,N′*-diisopropylactamidinate)/H_2O cycles. Perfect zero-mismatched epitaxy was achieved on GaAs(111)A by depositing $La_{1.7}Y_{0.3}O_3$, as shown in Figure 3. The effects of mismatch on the electrical properties of epi-$LaYO_3$ on GaAs(111)A were studied. These results suggest that atomic layer epitaxy of rare-earth oxides/GaAs(111)A is a promising structure for future generations of high-power/high-frequency analog devices or high-speed logic devices.

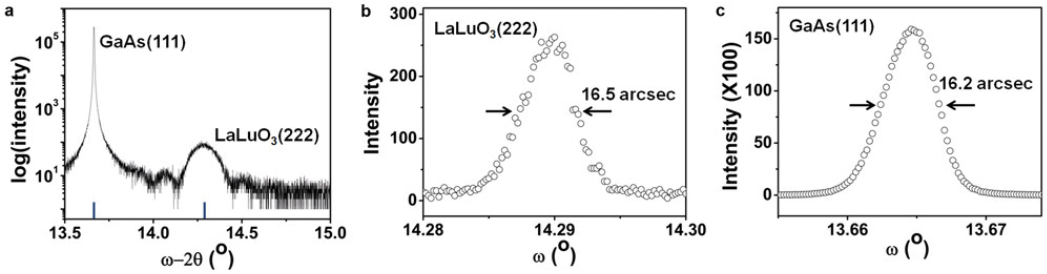

Figure 1 (a) High-resolution X-ray omega-two theta scan for $LaLuO_3$ film on GaAs(111)A. (b) and (c) The rocking curves of the $LaLuO_3$ (222) peak and the GaAs(111) peak, respectively.

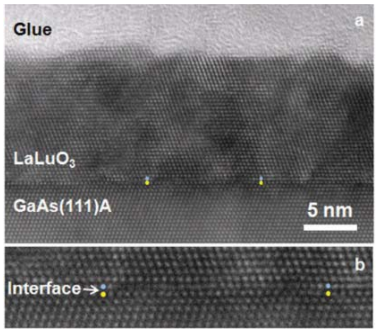

Figure 2 (a) Cross-sectional TEM of $LaLuO_3$/GaAs(111)A heterostructure. (b) A magnified image of the interface.

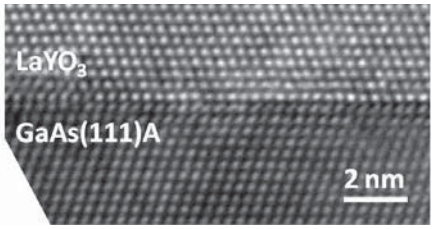

Figure 3. Cross-sectional TEM of $La_{1.7}Y_{0.3}O_3$/GaAs(111)A. The mismatch is zero for this composition with 15% Y_2O_3

Atomic Layer Epitaxy of Rare Earth Oxide Films on GaAs and Device Properties

2011 ALD Meeting

Yiqun Liu[1)], Min Xu[2)], Jaeyeong Heo[1)], Peide D. Ye[2)], and Roy G. Gordon[1)]

1) Department of Chemistry and Chemical Biology, Harvard University
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Motivation

- **High-κ and high mobility for future scaling**
- **GaAs: high electron mobility**
- **Issue: small I_{DS} in GaAs NMOSFET ← Fermi-level pinning**
- **Fermi-level unpinning: GaAs(111)A with ALD Al_2O_3*** ***(Prof. Ye's group at Purdue)***

* "Metal-oxide-semiconductor field-effect transistors on GaAs (111)A surface with atomic-layer-deposited Al_2O_3 as gate dielectrics." M. Xu, Y. Q. Wu, O. Koybasi, T. Shen, and P. D. Ye, *Appl. Phys. Lett.* 94, 212104 (2009).

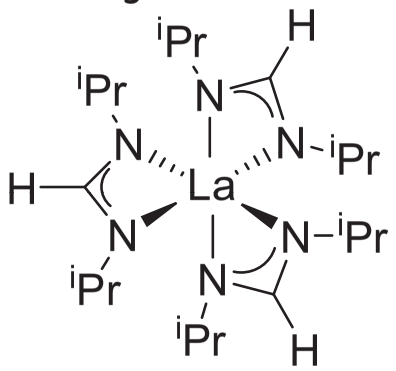
High-κ on GaAs for EOT scaling

on GaAs	κ	Band gap (eV)	ΔEc (eV)	ΔEv (eV)
Al_2O_3	8	6.5	1.8	3.4
HfO_2	12	6.2	1.8	3
$LaAlO_3$	15	5.8	1.6	2.8
$GdScO_3$	22	5.7	2	2.3
$LaScO_3$	23	5.6	2	2.3
$LaLuO_3$	32 (bulk)	5.6	2.1	2.2

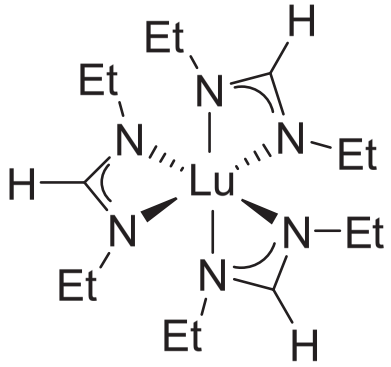
"Band offsets of high K gate oxides on III-V semiconductors" J. Robertson and B. Falabretti, *J. Appl. Phys*. 100, 014111(2006)

ALD process for $LaLuO_3$ films

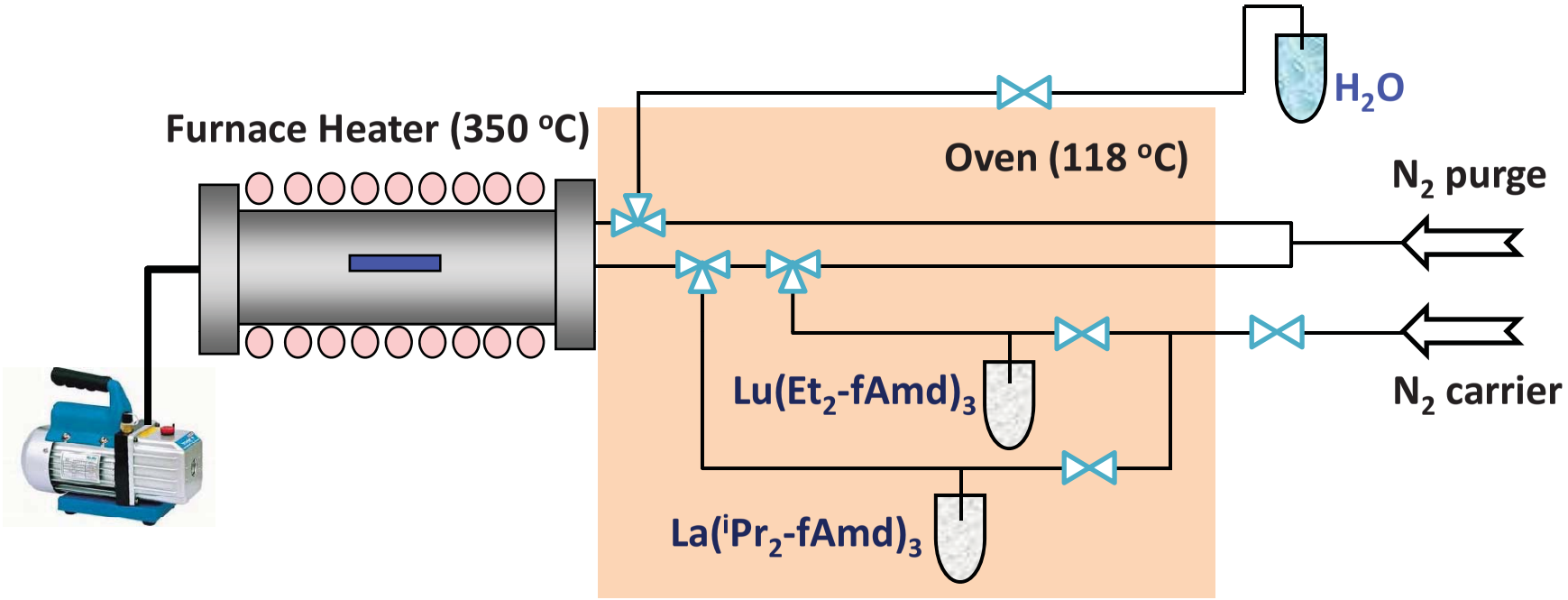
- **Metal amidinate precursor for ALD La_2O_3:**
  - **Lanthanum tris(*N,N'*-diisopropylformamidinate) or La($^{i}Pr_2$-fAmd)$_3$**
  - **white solid**
  - **most volatile La compound known, 60 mTorr at 100 °C**
  - **high reactivity to H_2O, O_2 and NH_3**



- **Metal amidinate precursor for ALD Lu_2O_3:**
  - **Lutetium tris(*N,N'*-diethylformamidinate) or Lu(Et_2-fAmd)$_3$**
  - **more volatile than La($^{i}pr_2$-fAmd)$_3$**



ALD process for $LaLuO_3$ films

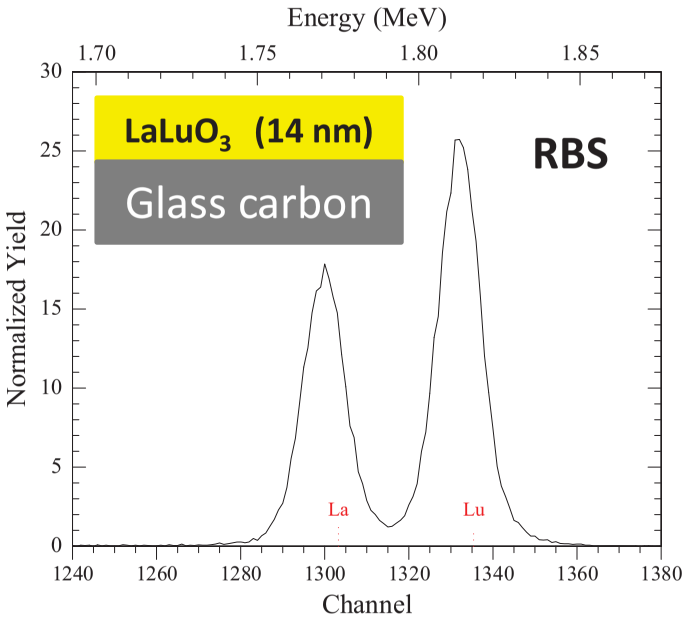


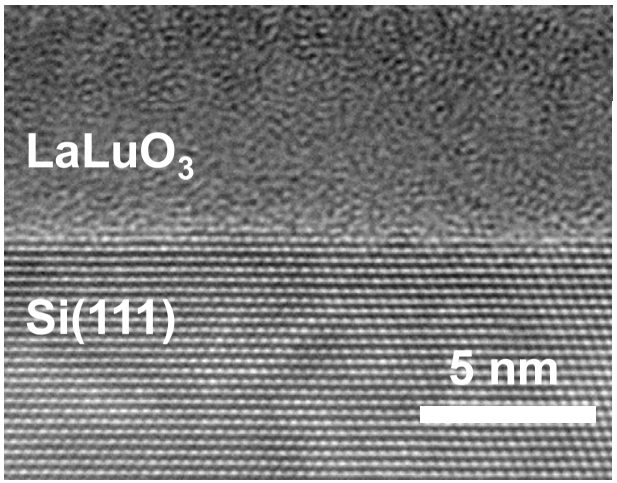
ALD process condition for $LaLuO_3$

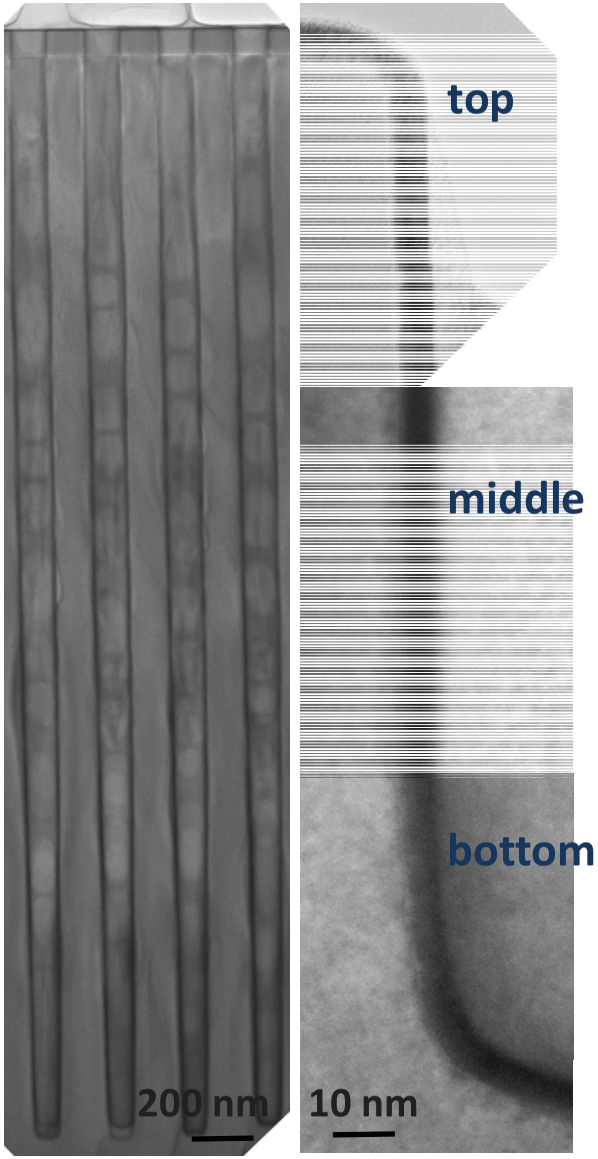
MO precursors	Oxidant	Bubbler temp.	Deposition temp.	La_2O_3 : Lu_2O_3	Exposure
$La(^iPr_2\text{-}fAmd)_3$ $Lu(Et_2\text{-}fAmd)_3$	DI H_2O	118 °C	300-350 °C	1:1	0.003 Torr s for metal precursor 0.06 Torr s for H_2O

Properties of ALD $LaLuO_3$

- **Composition (RBS)**
  - La:Lu=1:0.9
  - 80% of bulk density
  - C and N not detectable
- **Amorphous on Si with abrupt interface (κ ~26)**
- **Highly conformal (90% step coverage)**



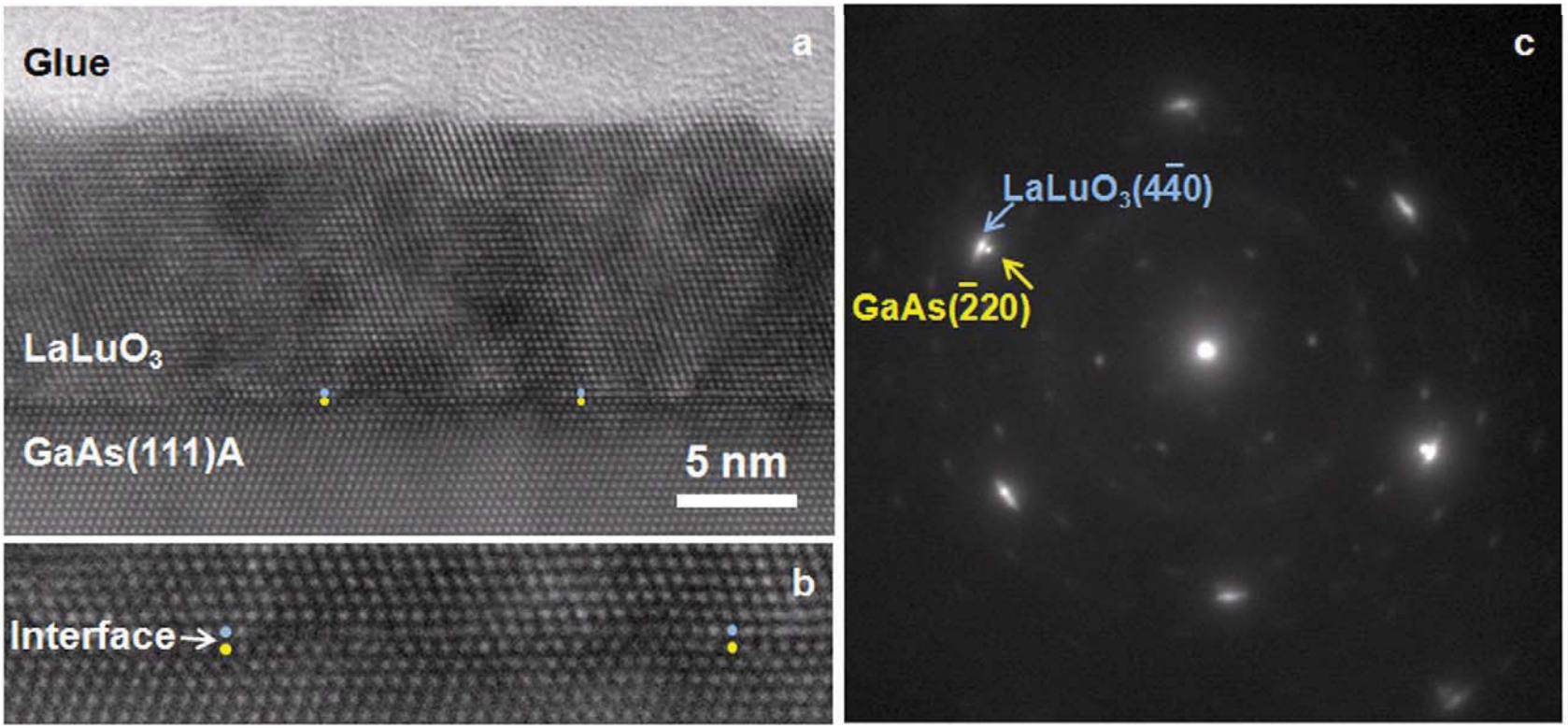




TEM, aspect ratio: 65:1*

*H. Wang, J.-J. Wang, R. Gordon, J.-S. M. Lehn, H. Li, D. Hong, and D. V. Shenaic, Electrochem. Solid-State Lett. 12, G13 (2009).

Properties of ALD $LaLuO_3$ on GaAs(111)A



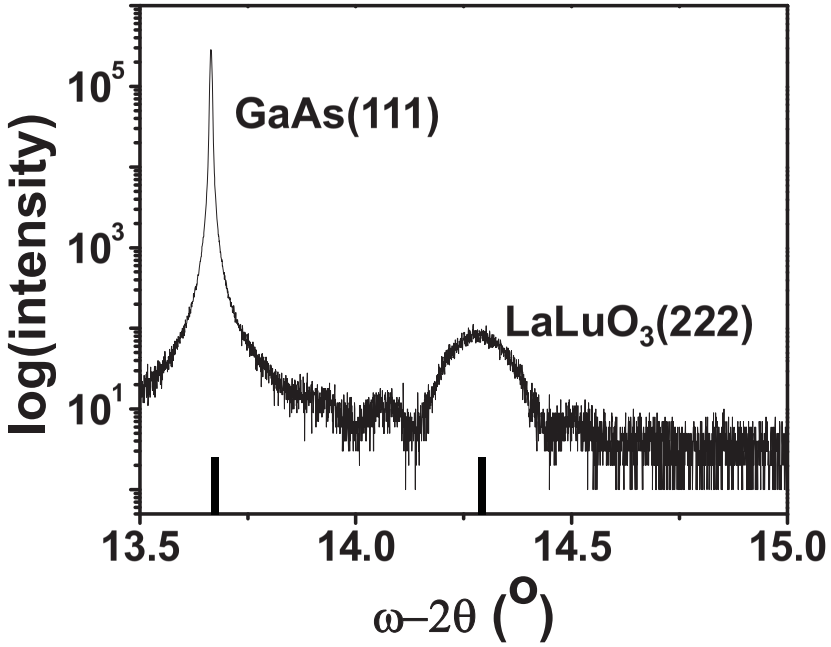
- **Lattice mismatch ~-4%***
- **Relaxed**
- **Epitaxy: cubic, not orthorhombic!**

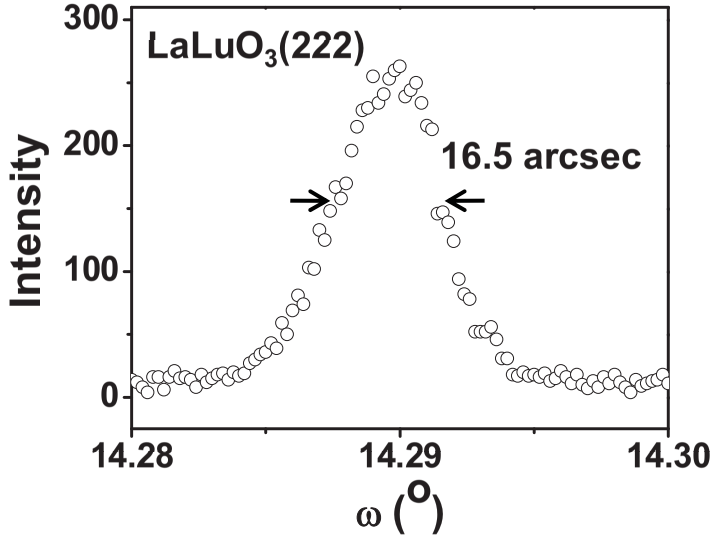
** defined as $(a_{oxide}-2a)/2a$*

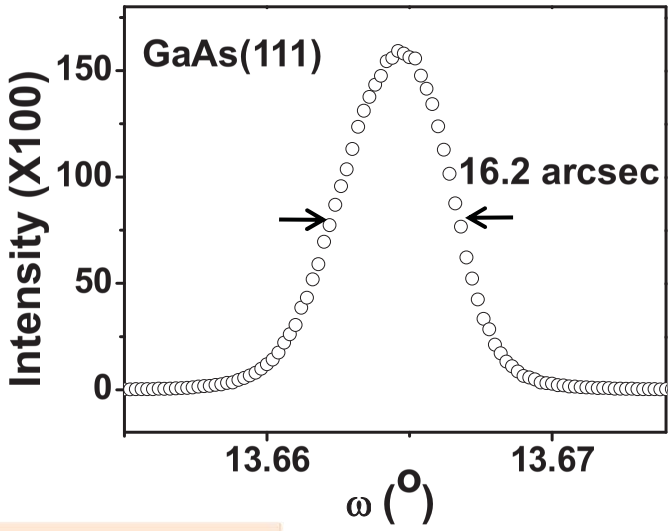
"Hetero-epitaxy of single-crystal $LaLuO_3$ on GaAs(111)A by atomic layer deposition" Yiqun Liu, Min Xu, Jaeyeong Heo, Peide D. Ye, and Roy G. Gordon, *App. Phys. Lett.* 97, 162910 (2010).

Quality of ALD epi-$LaLuO_3$ on GaAs(111)A

- High-resolution XRD measurements



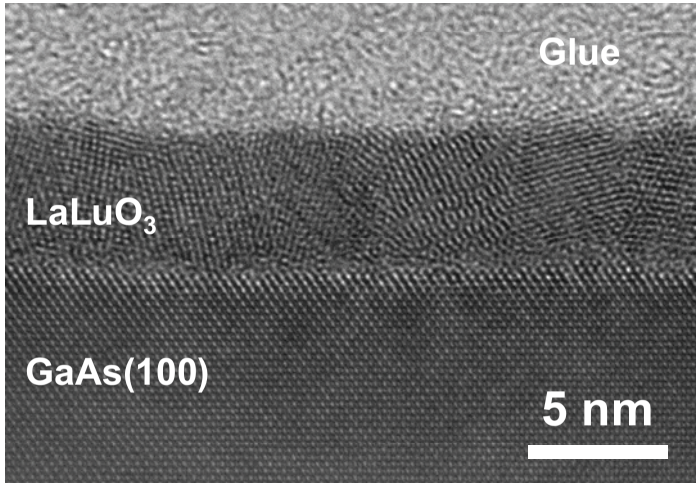


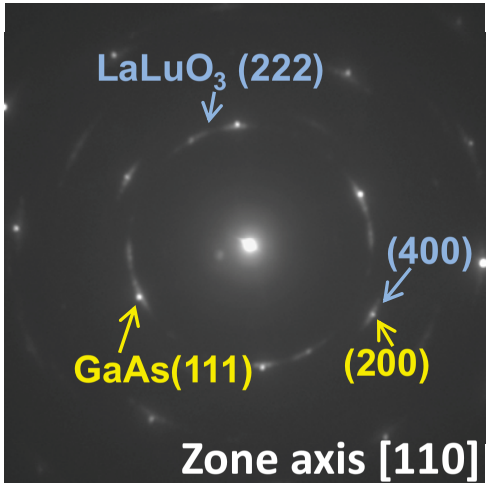


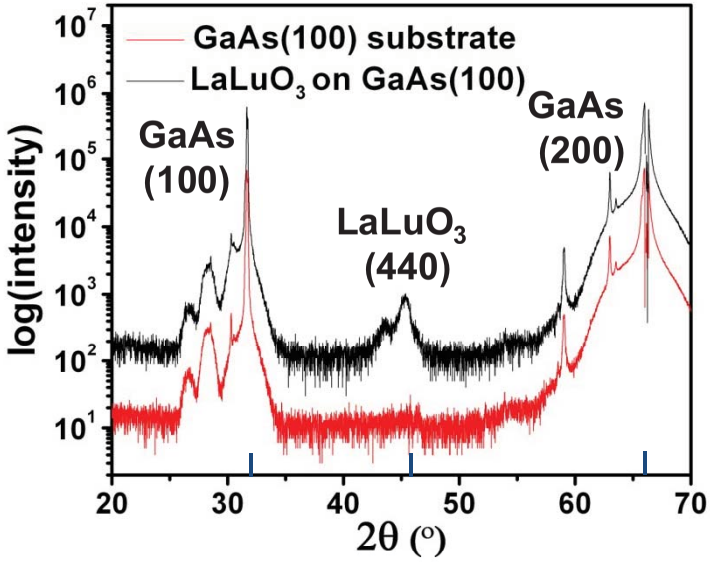
- Mismatch ~-3.8%
- Crystalline uniformity
- FWHM of the film peak

The quality of epitaxy is comparable to GaAs

Substrate-dependent crystal structures



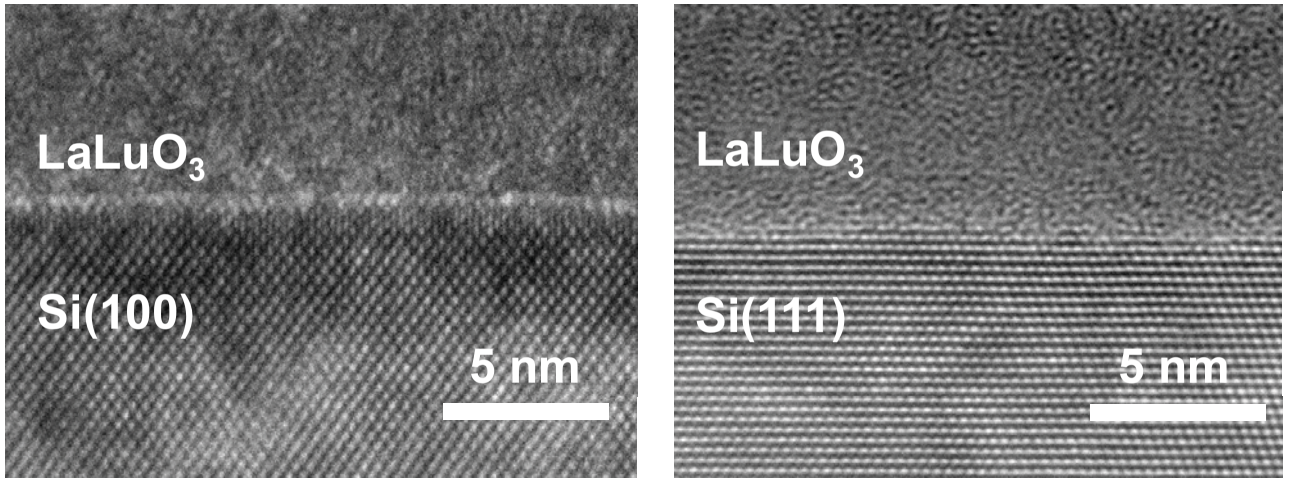




- **Cubic polycrystalline with (110) preferential orientation on GaAs(100)**

Yiqun Liu, Min Xu, Jaeyeong Heo, Peide D. Ye, and Roy G. Gordon, *App. Phys. Lett.* 97, 162910 (2010).

Substrate-dependent crystal structures



- **Amorphous on Si (0.18% mismatch)**
  - Silicate IL formation → Disturb ordering of substrate.

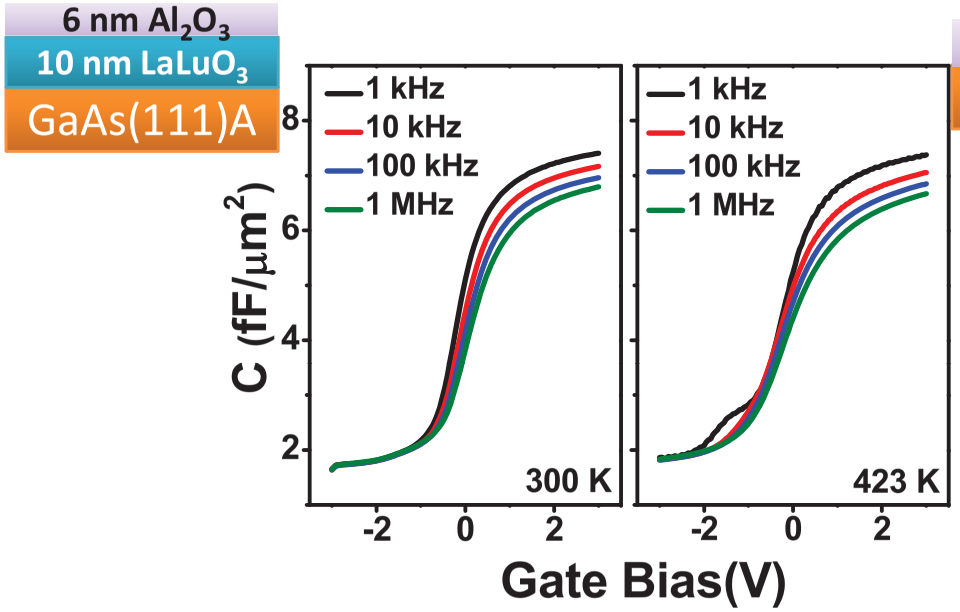
Epi-$LaLuO_3$/GaAs(111)A: no amorphous IL desirable for EOT scaling

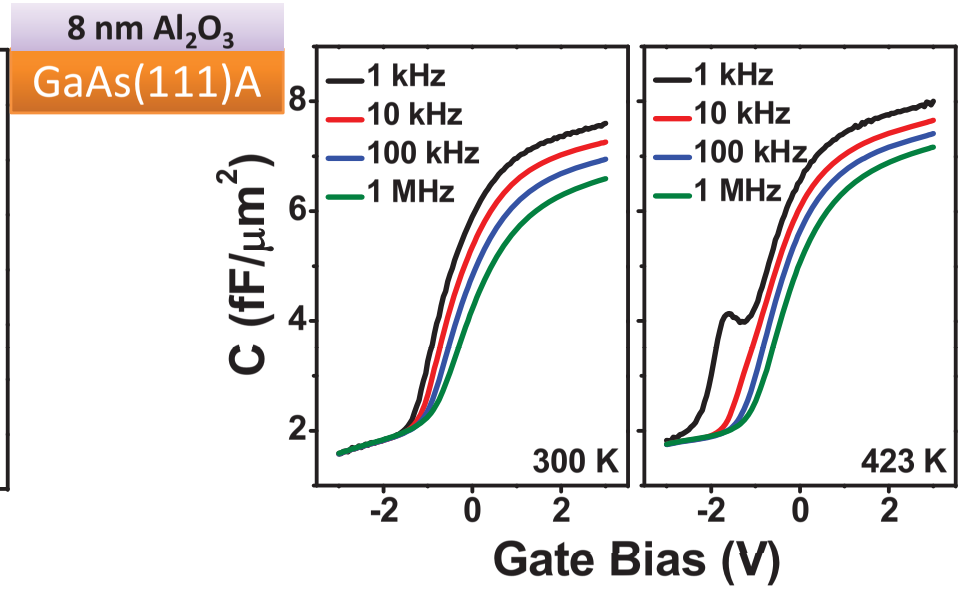
[1] J. Kwon, M. Dai, M. D. Halls, E. Langereis, Y. J. Chabal, and R. G. Gordon, *J. Phys. Chem. C* 113, 654 (2009).

[2] Yiqun Liu, Shaoping Shen, Leonard J. Brillson, and Roy G. Gordon, , *App. Phys. Lett.* 98, 122907 (2011).

Electrical properties

- Epi-$LaLuO_3$ v.s. a-Al_2O_3 on GaAs(111)A



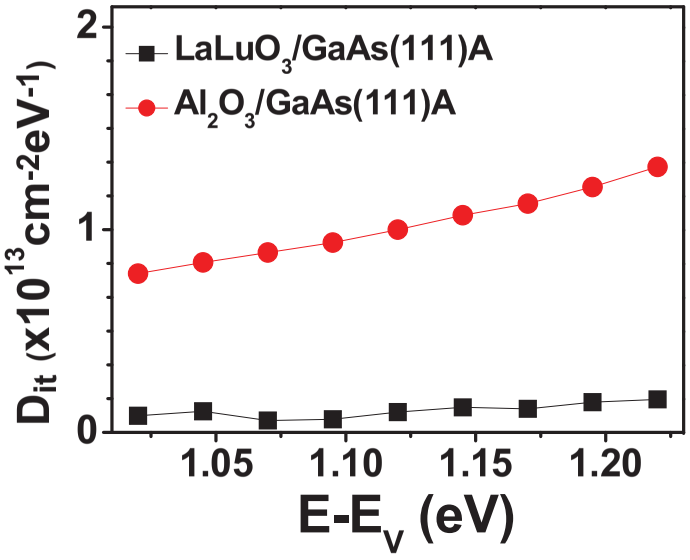


✓Dielectric constant is ~30

✓Smaller V_{FB} & frequency dispersions

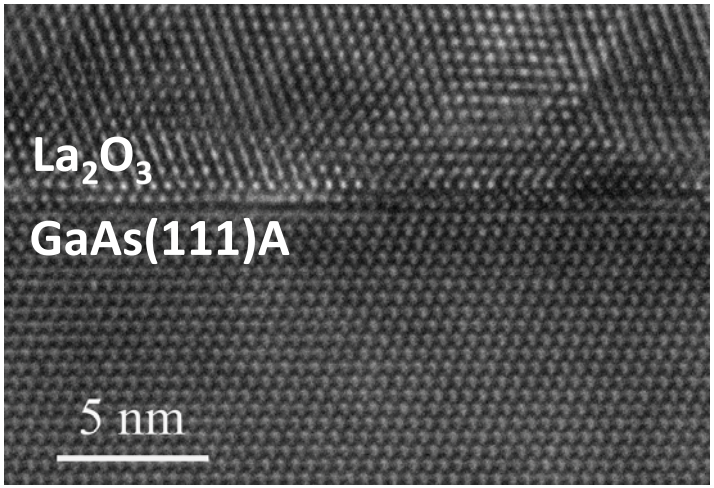
✓Interface state density (D_{it}) ~ 7×10^{11} cm^{-2} eV^{-1}

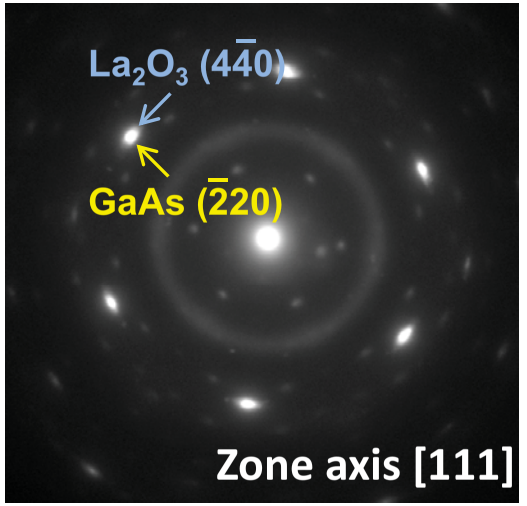
$LaLuO_3$/GaAs(111)A : *better interface*



Lattice mismatch engineering

- ALD La_2O_3 on GaAs(111)A
  - nearly zero lattice mismatch (+0.8%)
  - cubic phase (*not tetragonal*), κ~23





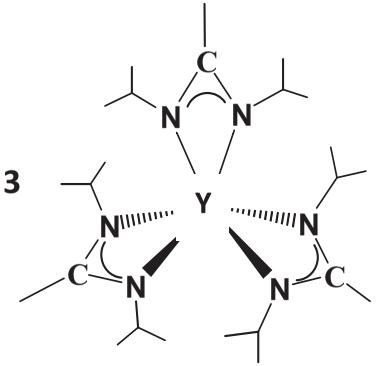
Lattice mismatch engineering

a_{Y2O3} =1.061 nm
a_{La2O3} =1.141 nm
$2*a_{GaAs}$ = 1.130 nm

Sc													
Y													
La													
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu

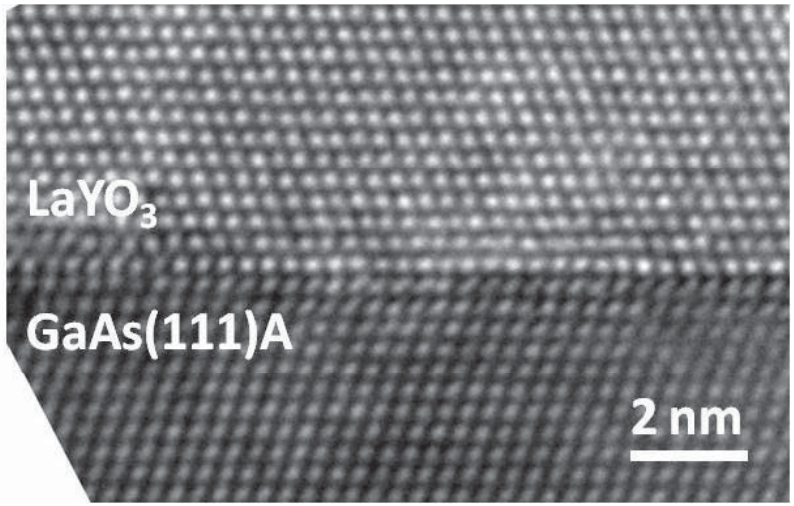
Adjust lattice parameters to get perfect lattice match

- **Metal amidinate precursor for ALD Y_2O_3**
  - **Yttrium tris(*N,N'*-diisopropylacetamidinate) or $Y(^iPr_2\text{-amd})_3$**
  - **White solid, less volatile**



- **ALD $LaYO_3$ @300 °C**

Subcycle ratio $La_2O_3 : Y_2O_3$	Composition	Lattice mismatch
1:0	La_2O_3	+0.8%
3:1	**$La_{1.7}Y_{0.3}O_3$**	**0**
1:2	$La_1Y_1O_3$	-2.5%
0:1	Y_2O_3	-6%



Summary

- **Substrate-dependent structures of ALD $LaLuO_3$**
  - Epitaxy on GaAs(111)A
  - Poly. on GaAs(100)
  - Amorph. on Si
- **Promising electrical properties of epi-$LaLuO_3$/GaAs(111)A**
  - High κ and low D_{it}
  - Fermi-level is unpinned
- **Lattice mismatch engineering**
  - $La_{1.7}Y_{0.3}O_3$ on GaAs(111)A: perfect lattice match

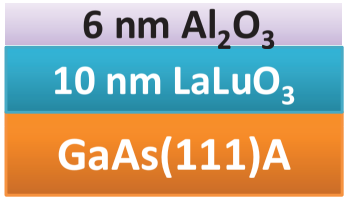
Acknowledgements

- Prof. Roy Gordon
  and all group members

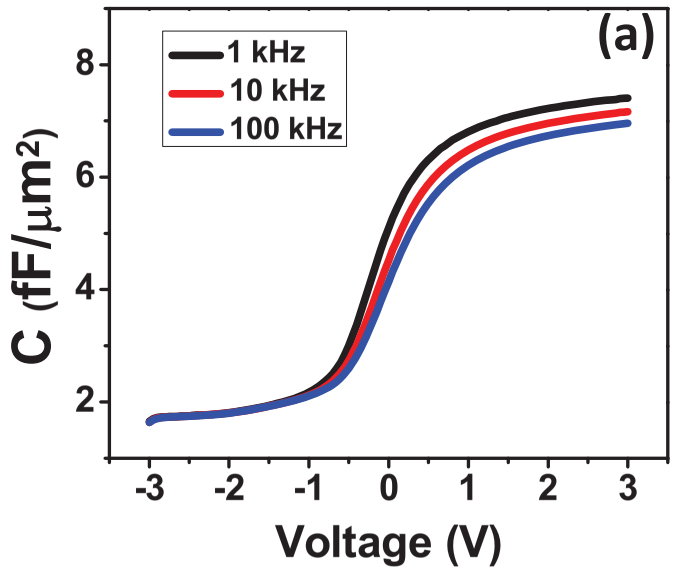
- Prof. Peide D. Ye and Min Xu
- Dr. Jun-Jieh Wang prepared Lu precursor
- Dow Chemical provides La and Y precursor
- Center for Nanoscale Systems (CNS) at Harvard

Electrical properties

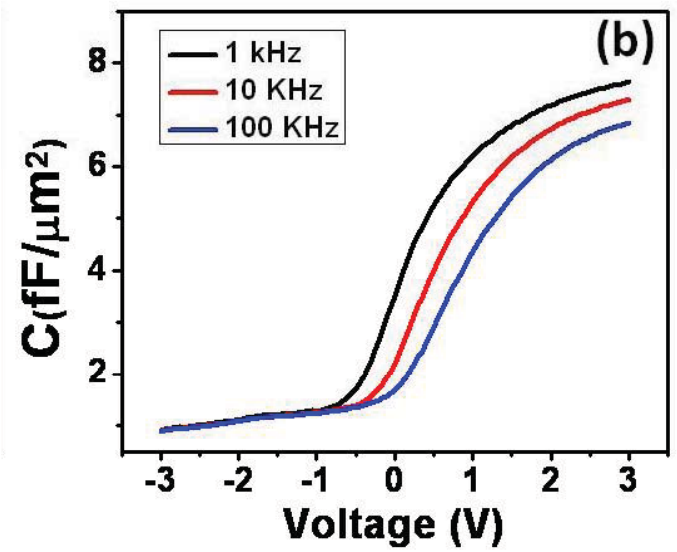
- **Effect of sulfur passivation**



Sulfur passivation



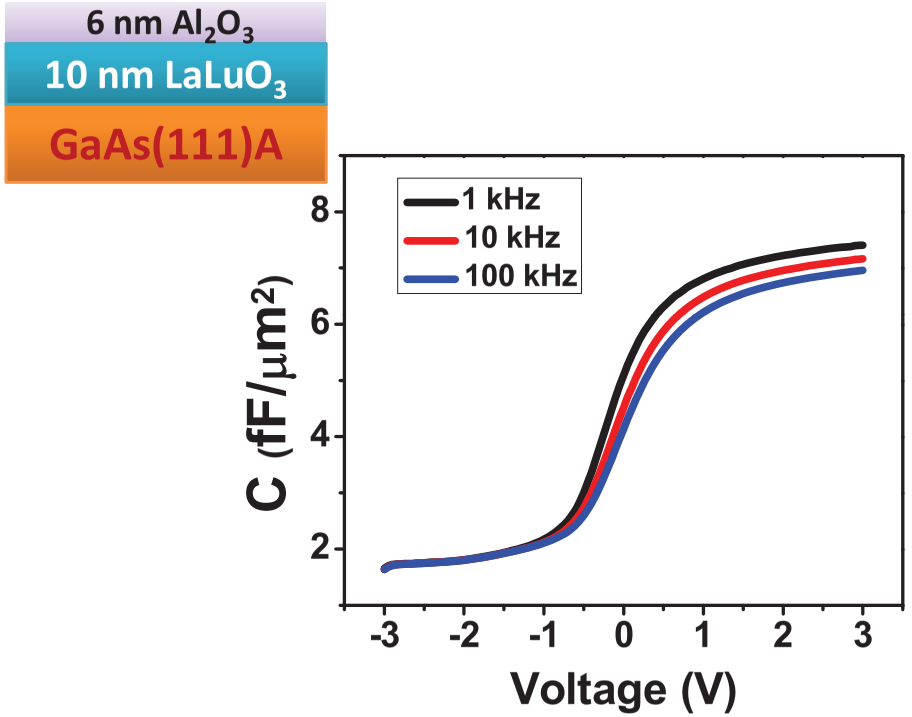
Without passivation

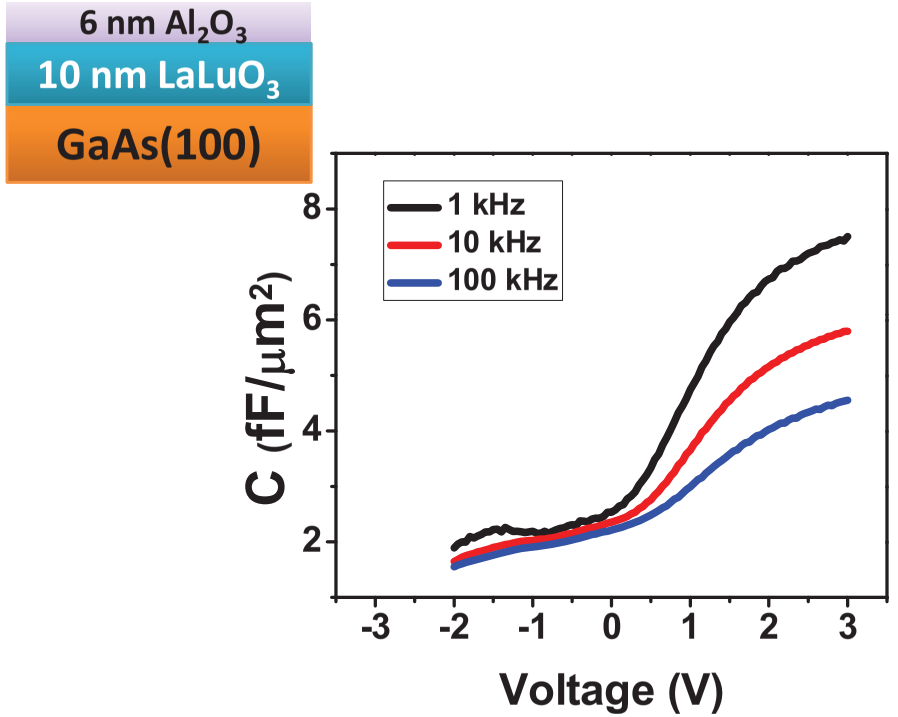


All devices: RTA in N_2 at 700 ^oC before Ni electrodes were patterned on the devices.

Electrical properties

- GaAs(111)A v.s. GaAs(100)





- ❑ Fermi-level is <u>partially pinned</u> and D_{it} is higher on GaAs(100).
- ❑ Fermi-level is <u>unpinned</u> on GaAs(111)A.